

TEMPERATURE PROGRAMMED SOLUBILIZATION OF COAL: CHARACTERIZATION OF PRODUCT FRACTIONS

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INTRODUCTION

For more than forty years, it has been recognized that the many interactive physical and chemical phenomena which comprise coal liquefaction fall into two functional categories: productive processes and counter-productive processes (1,2,3). Yet despite this understanding, the nature of these components and the contribution of each to the overall conversion have remained obscure. This can be attributed, in part, to the complex nature of coal but is also due to poor perception of the problem and to consequent deficiencies in experimental design.

The conversion of coal to liquid products is clearly a dynamic process. It is, therefore, quite curious that most coal scientists continue to employ investigative techniques more appropriate for measuring thermodynamic rather than dynamic phenomena. These techniques confine starting materials, intermediates, and products to the same reaction space throughout the primary product-determining segment of the conversion.

From this perspective, autoclaves (4,5), tubing bombs (6), and even staged flow reactors (7) are simply incapable of resolving productive and counter-productive processes. In these reactor systems, secondary processes are promoted rather than inhibited and, thus, obscure primary pathways in the conversion. Interpretations of the results from these experiments in terms of primary processes are beyond the capacities of mere mortals. On the other hand, fixed bed, flow mode reactors have the capacity to remove conversion products as they dissolve in the flowing phase; and, in this way, such reactors inhibit secondary reactions involving solubilized products.

Recently, we reported the development of a flow mode micro-reactor for the purpose of dynamically investigating the thermal dissolution of coal (8). Using this apparatus, we established characteristic staged temperature solubilization profiles for coals of various ranks and presented evidence that these dynamic profiles were comprised of (at least) two types of solubilization phenomena. In the present study, we have confirmed and extended these findings by using temperature programmed experiments to clearly resolve the benzene solubilization events and by characterizing the coal liquids produced during these events.

EXPERIMENTAL

General

Illinois No. 6 Coal from the Ames Laboratory Coal Library was used for these studies. The ultimate analysis for this coal (dmmf basis) is C: 80.60%; H: 5.63%; N: 1.56%; S_{org}: 2.35%; and O(diff): 9.81%. Ash (dry basis) and volatile matter (dmmf basis) contents are 10.0% and 40.4%, respectively. Prior to use, the coal was ground, sized to 200 x 400 mesh, riffled to insure uniformity, and dried at 110°C overnight under vacuum. Degassed HPLC grade benzene was used in the solubilization experiments; and samples and solvents were handled and stored under nitrogen.

Solubilization Procedures

Flow mode solubilization experiments were carried out in an improved version of our flow mode reactor. New features include continuous, "on-line" optical density monitoring of the reactor effluent; real time data acquisition of optical density, temperature, and pressure; and an improved time resolved product collection system. In a typical experiment, a preweighed amount (25-200 mg) of 200-400 mesh coal was placed in the tubular reactor, fixed in place by 2 μ stainless steel frits, and a shielded 0.062 inch o.d. chromel-alumel thermocouple was inserted into the coal bed. After connecting the reactor and purging the apparatus with nitrogen, the entire system was filled with benzene and pressurized to 3190 psi before adjusting the solvent flow to 1.0 ml/minute.

Two kinds of temperature programmed benzene solubilization experiments were carried out:

- (1) Staged temperature benzene solubilization and
- (2) Continuous temperature benzene solubilization.

In the former experiments, targeted temperatures were always attained and stabilized within 3 to 5 minutes. For all experiments, temperature was controlled during the conversion according to a predetermined program; and the optical density profile of the product stream, as well as temperature and pressure profiles of the coal bed, were recorded throughout the conversion. Products were collected at appropriate times on the basis of the optical density profile.

Chromatographic Analysis of Products

Samples were prepared for analysis by removing the solvent from the solubilization product at room temperature using a slow stream of nitrogen. The dried product was then dissolved in 0.2 ml of tetrahydrofuran and this solution was used for chromatographic analysis. Products were analyzed by Reverse Phase Liquid Chromatography (RPLC) on a 4.1 mm x 300 mm μ -Bondapak (phenyl/corasil) column (Alltech Associates), by Gel Permeation Chromatography (GPC) on 1000, 500, and 100 Angstrom μ -Styragel columns (Waters Associates), and by Capillary Gas Chromatography on a 30 meter DB-5 column (J&W Scientific).

RESULTS & DISCUSSION

Solubilization Profiles

Previous investigations in our laboratories (9) have provided persuasive evidence that coal solubilization in benzene proceeds via physical processes at temperatures below 300°C and that, as the temperature is increased beyond 300°C, thermal chemical processes become progressively more important. Staged temperature, flow mode experiments have proven useful as a means of investigating solubilization phenomena as a function of time and temperature (8). A staged temperature (260/390°C) solubilization profile for Illinois No. 6 coal is shown in Figure 1.

Under these conditions, it is not clear whether the maxima in effluent absorbance at 3 minutes and 24 minutes are due to distinct and resolvable conversion phenomena. The maxima coincide with heating ramps and could simply reflect a general temperature driven increase in all of the processes which contribute to solubilization. This question was addressed by carrying out the benzene solubilization experiment while programming the temperature continuously from 25°C to 420°C (Figure 2). The solubilization profile generated in this manner demonstrates conclusively that there are at least two distinct solubilization events: one in the 240 to 280°C region and the other in the 370-410°C region.

Characterization of Products

In order to further investigate the nature of these events, low temperature product (LTP) and high temperature product (HTP) fractions were collected during the times indicated in Figure 2. These fractions were then analyzed by Reverse Phase Liquid Chromatography (RPLC) and by Gel Permeation Chromatography (GPC), and the resulting chromatograms are shown in Figures 3 and 4, respectively. On the basis of RPLC, the High Temperature Fraction appears to have a larger polar component than the Low Temperature Fraction. However, these results are not unambiguous; the difference in RPLC patterns appears to be due to differences in the relative concentrations of components rather than the presence or absence of components in the product fractions. Furthermore, little difference is apparent in the GPC traces of the two fractions (Figure 4).

To clarify these results, products were collected from a three stage (260/340/420°C) solubilization experiment and analyzed by RPLC and GPC (Figures 5 and 6). The chromatograms reveal unambiguous differences in the products and provide the basis for two important conclusions. That the material produced at 420°C is distinctly more polar than products solubilized at lower temperatures is clear from the RPLC traces (Figure 5). It is equally apparent from the GPC traces (Figure 6) that the molecular weight of the product increases to a maximum between 260 and 420°C.

Thus, while the molecular weight distributions of the products at 260 and 420°C are quite similar (see also Figure 4), the products themselves are almost certainly generated by different

processes. It appears that the 260°C fraction is produced by physical dissolution processes which continue to dominate pyrolytic processes at 340°C. However, by 420°C, thermal chemical fragmentation processes are dominant and the average MW of the product has decreased while the polarity has increased.

FUTURE WORK

We have begun to test this hypothesis and to further elucidate the nature of these processes using GC/MS to analyze time and temperature resolved products from our experiments. In Figure 7, the capillary gas chromatograms of the 260 and 420°C fractions are compared with those of acetone extracts from whole coal and coal tar (420°C, vacuum). Major new components, absent in the low temperature extracts are apparent in both 420°C products and are now being analyzed by GC/MS.

ACKNOWLEDGEMENT

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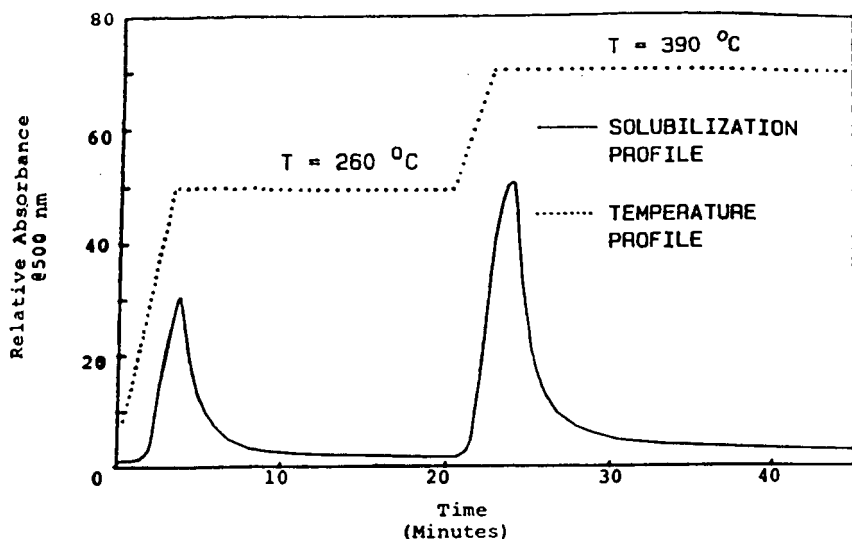


Figure 1. Staged Temperature Benzene Solubilization of Illinois No. 6 Coal. First Stage: $260^{\circ}\text{C}/3180$ psi; Second Stage: $390^{\circ}\text{C}/3180$ psi.

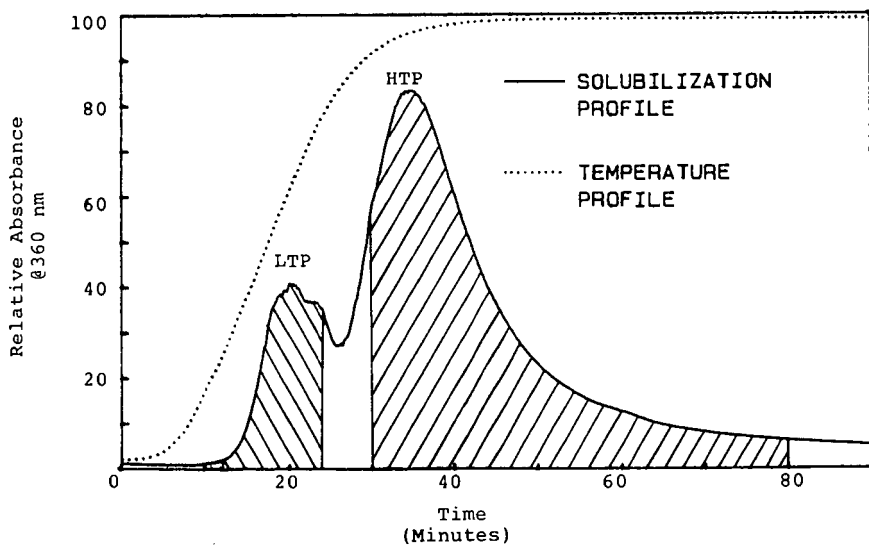


Figure 2. Continuous Temperature Benzene Solubilization of Illinois No. 6 Coal at 3180 psi. Initial Temperature: 20°C ; Final Temperature: 420°C .

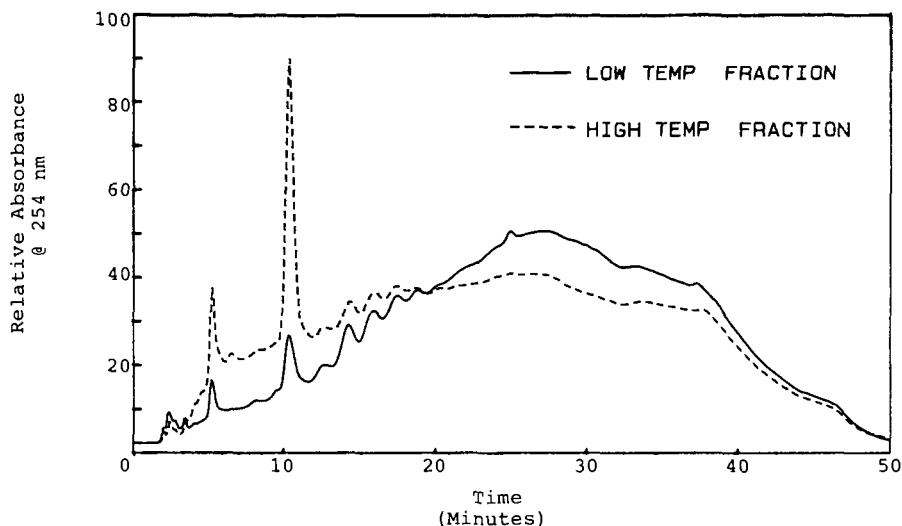


Figure 3. Liquid Chromatograms of Products from the Continuous Temperature Programmed Benzene Solubilization of Illinois No. 6 Coal.

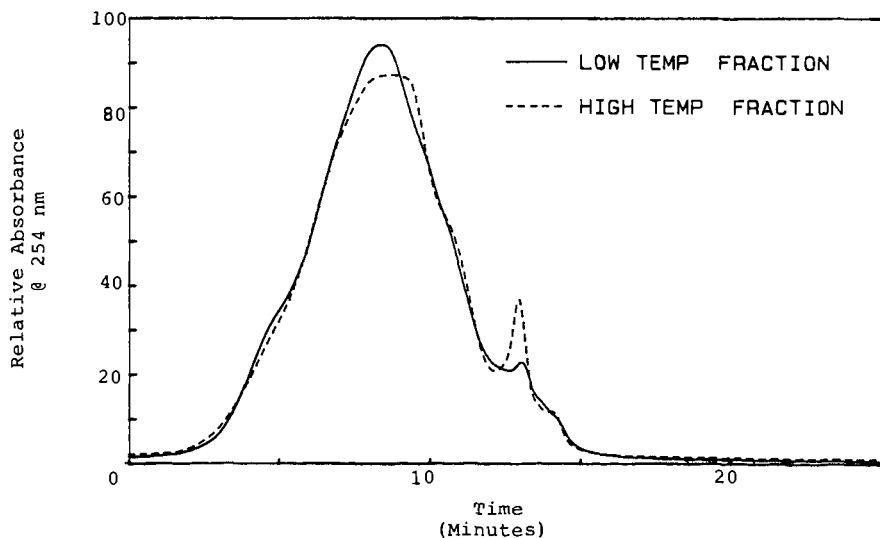


Figure 4. Gel Permeation Chromatograms of Products from the Continuous Temperature Programmed Benzene Solubilization of Illinois No. 6 Coal.

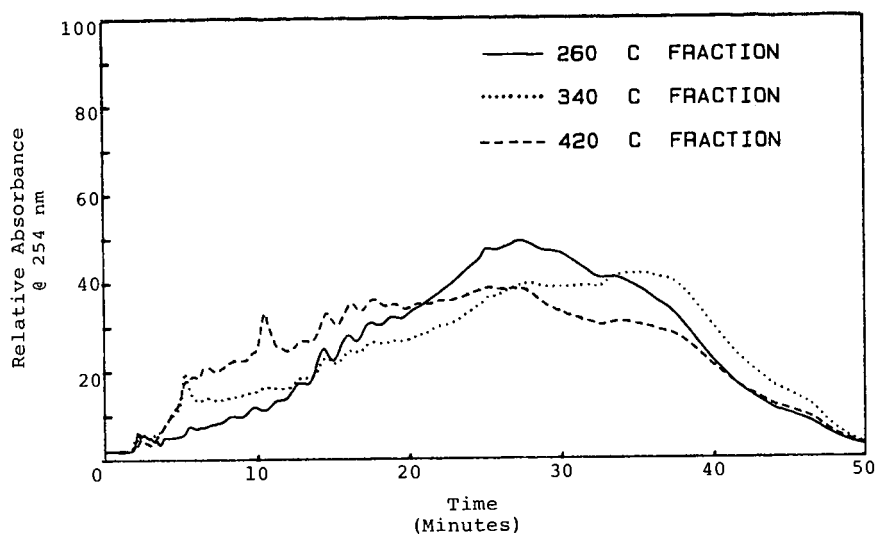


Figure 5. Liquid Chromatograms of Products from the Temperature Staged Benzene Solubilization of Illinois No. 6 Coal.

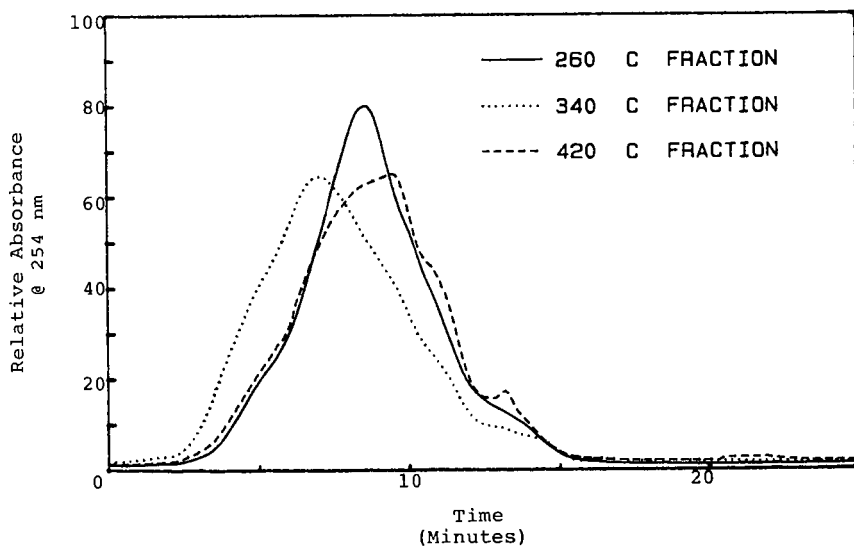


Figure 6. Gel Permeation Chromatograms of Products from the Temperature Staged Benzene Solubilization of Illinois No. 6 Coal.

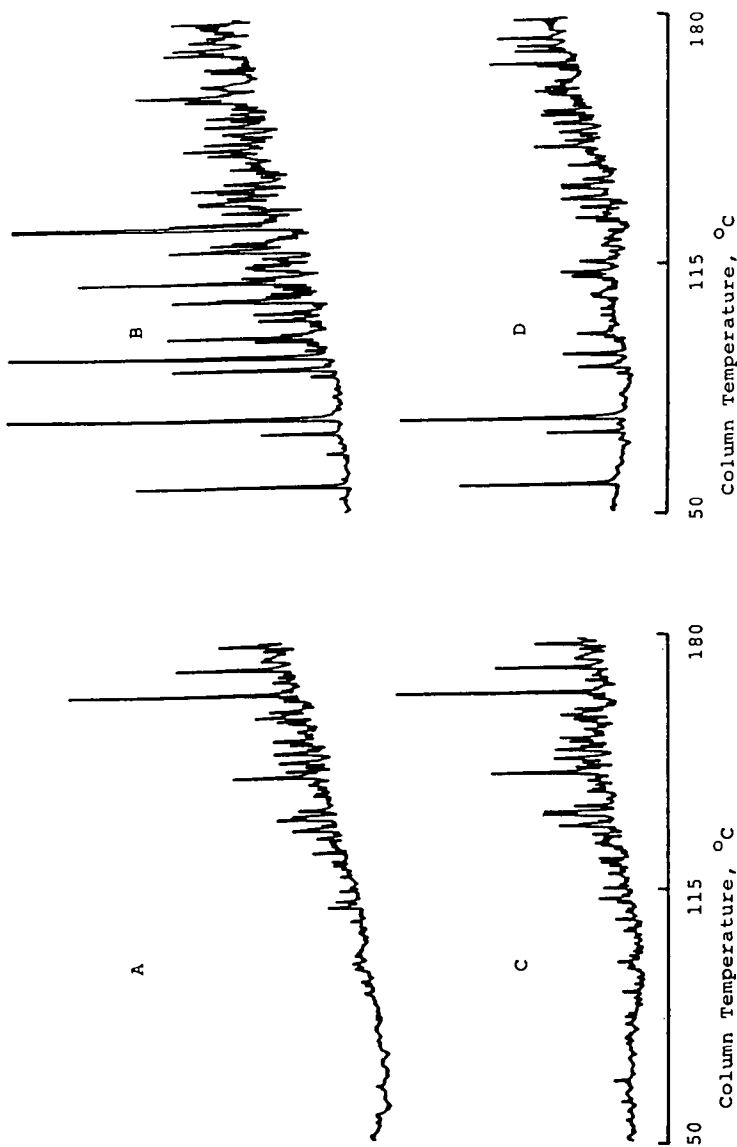


Figure 7. Capillary Gas Chromatography Data for the Benzene Solubilization and Pyrolysis Products from Illinois No. 6 Coal. A - Solubilization at 260 °C; B - Solubilization at 420 °C; C - Room Temperature Acetone Extract; D - Pyrolysis at 420 °C (Acetone Soluble Tar).